JC13 Rec'd PCT/PTO 2 3 JUL 2001

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(REV 12-29-99)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 36 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
BDL-341XX

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
09/889860

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/03275	24 November 2000 (24.11.00)	24 November 1999 (24.11.99)

TITLE OF INVENTION
A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, IN PARTICULAR FOR AN INSTALLATION THAT PRODUCES SILICON SINGLE CRYSTALS

APPLICANT(S) FOR DO/EO/US
Jean-Michel Georges; Daniel Benethuiliere; Eric Philippe

Applicant herewith submits to the United states Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:
    FORMAL DRAWINGS (3 sheets)
    VERIFICATION OF TRANSLATION

Express Mail Number
EL 751779448 US

JC18 Rec'd PCT/PTO 2 3 JUL 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/889860	INTERNATIONAL APPLICATION NO PCT/FR00/03275	ATTORNEY'S DOCKET NUMBER BDL-341XX

	CALCULATIONS	PTO USE ONLY
17. [X] The following fees are submitted: **BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1,000.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00** International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00** International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	CALCULATIONS	PTO USE ONLY
Total claims	24 - 20 =	4	X **$18.00**	$ 72.00	
Independent claims	1 - 3 =	0	X **$80.00**	$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			**+$270.00**	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 932.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				$ --	
SUBTOTAL =				$ 932.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$ 0	
TOTAL NATIONAL FEE =				**$ 932.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property				$ 40.00	
TOTAL FEES ENCLOSED =				$ 972.00	
				Amount to be refunded:	$
				charged:	$

a. [X] A check in the amount of $ 932.00 to cover the above fees is enclosed. A check in the amount of $ 40.00 is enclosed for the assignment recordation fee.

b. ☐ Please charge my Deposit Account No. ________ in the amount of $ ________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0804 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Customer Number 207

SEND ALL CORRESPONDENCE TO:

Weingarten, Schurgin, Gagnebin & Hayes LLP
Ten Post Office Square
Boston, Massachusetts 02109

Date: 7-23-1

SIGNATURE

Charles L. Gagnebin III
NAME

25,467
REGISTRATION NUMBER

09/889860

PATENT

JC18 Rec'd PCT/PTO 23 JUL 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application	:	JEAN-MICHEL GEORGES, ET AL.
Application No.	:	
Filed	:	Herewith
For	:	A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, IN PARTICULAR FOR AN INSTALLATION THAT PRODUCES SILICON SINGLE CRYSTALS
Examiner	:	
Attorney's Docket	:	BDL-341XX

Group Art Unit:

* *

~~I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Commissioner for Patents, Washington, D.C. 20231 on ____________________.~~

~~By:____________________~~
~~Charles L. Gagnebin III~~
~~Registration No. 25,467~~
~~Attorney for Applicant(s)~~

* *

PRELIMINARY AMENDMENT

BOX PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly enter the following Preliminary Amendment in the above-identified application:

In the Claims:

Express Mail Number
EL 751779448 US

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Please amend the Claims to read as follows (a copy of the amended claims showing the additions and deletions appears at the end for the Examiner's convenience):

1. A method of manufacturing a bowl of thermostructural composite material formed by fiber reinforcement densified by a matrix, the method being characterized in that comprises the steps consisting in:

· making a bowl preform by winding a yarn, the preform having an axial passage through its bottom;

· densifying the bowl preform by chemical vapor infiltration; and

· closing the passage by means of a plug.

3. A method according to claim 1, characterized in that the consolidated bowl preform is made by winding a yarn impregnated by a precursor for said material constituting the matrix, and by transforming the precursor by heat treatment.

4. A method according to claim 3, characterized in that the consolidated bowl preform is made by winding a yarn impregnated by a carbon precursor and by transforming the precursor.

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6. A method according to claim 3, characterized in that two consolidated preforms are made simultaneously by winding a shape on a mandrel where the shape corresponds to that of two bowl outline portions joined rim-to-rim, and by cutting the resulting winding in its middle portion.

7. A method according to claim 1, characterized in that the bowl preform is made from yarn that has no surface treatment to provide surface functions.

8. A method according to claim 1, characterized in that the bowl preform is made from a carbon yarn.

9. A method according to claim 1, characterized in that the bowl is subjected to high temperature purification and stabilization treatment.

10. A method according to claim 1, characterized in that the high temperature purification and stabilization treatment is performed on the consolidated bowl preform.

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11. A method according to claim 9, characterized in that the purification and stabilization treatment is performed at a temperature greater than 2200°C.

12. A method according to claim 1, characterized in that bowl preform densification is performed by forming a carbon matrix.

13. A method according to claim 1, characterized in that the plug is made in two pieces that are assembled together so as to clamp onto the rim of the axial passage in the preform.

14. A method according to claim 1, characterized in that the passage is closed by a plug made of thermostructural composite material.

15. A method according to claim 1, characterized in that it includes a step consisting in performing a final chemical vapor infiltration step after the passage has been closed by the plug.

18. A method according to claim 1, characterized in that a protective coating is formed at least on the inside face of the bowl.

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21. A method according to claim 1, characterized in that the inside face of the bowl is provided with a protective layer.

Please add the following new claim 24:

24. A method according to claim 2, characterized in that:

the consolidated bowl preform is made by winding a yarn impregnated by a carbon precursor selected from phenolic, furan, epoxy, and polyimide resins for said material constituting the matrix, and by transforming the precursor by heat treatment;

two consolidated preforms are made simultaneously by winding a shape on a mandrel where the shape corresponds to that of two bowl outline portions joined rim-to-rim, and by cutting the resulting winding in its middle portion;

the bowl preform is made from yarn that has no surface treatment to provide surface functions;

the bowl preform is made from a carbon yarn;

the bowl is subjected to high temperature purification and stabilization treatment;

the high temperature purification and stabilization treatment is performed on the consolidated bowl preform;

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the purification and stabilization treatment is performed at a temperature greater than 2200°C;

bowl preform densification is performed by forming a carbon matrix;

the plug is made in two pieces that are assembled together so as to clamp onto the rim of the axial passage in the preform;

the passage is closed by a plug made of thermostructural composite material;

it includes a step consisting in performing a final chemical vapor infiltration step after the passage has been closed by the plug;

the final chemical vapor infiltration step comprises forming a ceramic matrix phase;

the ceramic matrix phase is made of silicon carbide;

a protective coating is formed at least on the inside face of the bowl;

a protective coating is made out of pyrolytic carbon or silicon carbide;

the inside face of the bowl is provided with a protective layer;

the protective layer is made of a thermostructural composite material; and

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a plurality of consolidated bowl preforms are densified simultaneously by chemical vapor infiltration.

REMARKS

This Preliminary Amendment puts the claims into proper form for examination.

Note that claims 1, 3, 4, 6-15, 18, and 21 have been amended; new claim 24 has been added; and claims 2, 5, 16, 17, 19, 20, 22, and 23 remain unchanged. Kindly calculate the filing fee based on the amended claims.

This Application contains a translation of the title and abstract as they were when originally filed by the Applicant. No account has been taken of any changes that may have been made subsequently by the PCT Authorities acting <u>ex officio</u>, e.g., under PCT Rules 37.2, 38.2, and/or 48.3.

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The Examiner is encouraged to telephone the undersigned attorney to discuss any matter which would expedite allowance of the present application.

Respectfully submitted,

JEAN-MICHEL GEORGES, ET AL.

By: ______________________
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Date: 7-23-1

CLG/mc/254789-1
Enclosure

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Red-lined claims for the Examiner's convenience:

1. A method of manufacturing a bowl of thermostructural composite material formed by fiber reinforcement densified by a matrix, the method being characterized in that comprises the steps consisting in:

· making a bowl preform ~~(28)~~ by winding a yarn, the preform having an axial passage ~~(30)~~ through its bottom;

· densifying the bowl preform by chemical vapor infiltration; and

· closing the passage by means of a plug ~~(34)~~.

3. A method according to claim 1 ~~or claim 2~~, characterized in that the consolidated bowl preform ~~(28)~~ is made by winding a yarn impregnated by a precursor for said material constituting the matrix, and by transforming the precursor by heat treatment.

4. A method according to claim 3, characterized in that the consolidated bowl preform ~~(28)~~ is made by winding a yarn impregnated by a carbon precursor and by transforming the precursor.

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6. A method according to ~~any one of~~ claims 3~~, 4, and 5~~, characterized in that two consolidated preforms are made simultaneously by winding a shape on a mandrel ~~(12)~~ where the shape corresponds to that of two bowl outline portions joined rim-to-rim, and by cutting the resulting winding ~~(22)~~ in its middle portion.

7. A method according to ~~any one of~~ claims 1~~ to 6~~, characterized in that the bowl preform is made from yarn that has no surface treatment to provide surface functions.

8. A method according to ~~any one of~~ claims 1~~ to 7~~, characterized in that the bowl preform is made from a carbon yarn.

9. A method according to ~~any one of~~ claims 1~~ to 8~~, characterized in that the bowl is subjected to high temperature purification and stabilization treatment.

10. A method according to ~~any one of~~ claims 1~~ to 8~~, characterized in that the high temperature purification and stabilization treatment is performed on the consolidated bowl preform.

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11. A method according to claim 9~~ or claim 10~~, characterized in that the purification and stabilization treatment is performed at a temperature greater than 2200°C.

12. A method according to ~~any one of~~ claims 1~~ to 11~~, characterized in that bowl preform densification is performed by forming a carbon matrix.

13. A method according to ~~any one of~~ claims 1~~ to 12~~, characterized in that the plug ~~(34)~~ is made in two pieces ~~(35, 37)~~ that are assembled together so as to clamp onto the rim of the axial passage in the preform.

14. A method according to ~~any one of~~ claims 1~~ to 13~~, characterized in that the passage ~~(30)~~ is closed by a plug ~~(34)~~ made of thermostructural composite material.

15. A method according to ~~any one of~~ claims 1~~ to 14~~, characterized in that it includes a step consisting in performing a final chemical vapor infiltration step after the passage ~~(30)~~ has been closed by the plug~~ (34)~~.

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18. A method according to ~~any one of~~ claims 1~~ to 17~~, characterized in that a protective coating is formed at least on the inside face of the bowl.

21. A method according to ~~any one of~~ claims 1~~ to 20~~, characterized in that the inside face of the bowl is provided with a protective layer.

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09/889860
JC18 Rec'd PCT/PTO 23 JUL 2001

APPLICANT: GEORGES Jean-Michel, BENETHUILIERE Daniel; PHILIPPE Eric

TITLE: A method of manufacturing a thermostructural composite material bowl, in particular for an installation that produces silicon single crystals.

U.S. COMPLETION OF

INTERNATIONAL APPLICATION PCT/ FR00/03275 FILED November 24, 2000

VERIFICATION OF A TRANSLATION

I, (name and address of translator) Barbara PELLIN of 158, rue de l'Université, 75007 PARIS - FRANCE hereby declare that:

My name and post office address are as stated above:

That I am knowledgeable in the English Language and the French Language and that I believe the English translation of the specification, claims, and abstract relating to International Application PCT/FR00/03275
filed November 24, 2000 is a true and complete translation.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(signature of translator)

Date April 24, 2001

Express Mail Number
EL 751779448 US

09/889860

JC18 Rec'd PCT/PTO 23 JUL 2001

Title of the invention

A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, IN PARTICULAR FOR AN INSTALLATION THAT PRODUCES SILICON SINGLE CRYSTALS.

Field of the invention

The invention relates to thermostructural composite material bowls. A field of application of the invention is more particularly manufacturing bowls for receiving crucibles containing molten metal, such as silicon.

The term "thermostructural composite material" is used to mean a material comprising fiber reinforcement made of refractory fibers, e.g. carbon fibers or ceramic fibers, and densified by a refractory matrix, e.g. of carbon or of ceramics. Carbon/carbon (C/C) composite materials and ceramic matrix composite (CMC) materials are examples of thermostructural composite materials.

Background of the invention

A well-known method of producing silicon single crystals in particular for manufacturing semiconductor products consists in melting silicon in a crucible, in putting a crystal germ having a desired crystal arrangement into contact with the bath of liquid silicon, so as to initiate solidification of the silicon contained in the crucible with the desired crystal arrangement, and in mechanically withdrawing an ingot of single crystal silicon obtained in this way from the crucible. This method is known as the Czochralski method or as the "CZ" method.

The crucible containing the molten silicon is usually made of quartz (SiO_2). The crucible is placed in a bowl which is generally made of graphite, it being understood that proposals have also been made to make the bowl at least in part out of C/C composite materials. The bottom of the bowl stands on a support. For this purpose, the bottom of the bowl must be machined, in

particular so as to form a bearing surface for centering purposes and also a support zone. In addition, in the application in question, very high purity requirements make it necessary to use raw materials that are pure, with methods that do not pollute them, and with methods of purification in the finished state or in an intermediate state of bowl manufacture. For carbon-containing materials (such as graphite or C/C composites), methods of purification by high temperature treatment (at more than 2000°C) under an atmosphere that is inert or reactive (e.g. a halogen) are known and are commonly used.

The pieces of graphite used as bowls are fragile. They are often made up of as a plurality of portions (so-called "petal" architecture) and they cannot retain molten silicon in the event of the crucible leaking. This safety problem becomes more critical with the increasing size of the silicon ingots that are drawn, and thus with the increasing mass of the liquid silicon. Furthermore, graphite bowls are generally of short lifetime while being thick and thus bulky. It is preferable to use C/C composite material pieces which do not present those drawbacks and which, in particular, present better mechanical properties.

The manufacture of a C/C composite material piece, or more generally a piece of thermostructural composite material, usually comprises making a fiber preform having the same shape as the piece that is to be made, and that constitutes the fiber reinforcement of the composite material, and then densifying the preform with the matrix.

Techniques presently in use for making preforms include winding yarns by coiling yarns on a mandrel having a shape that corresponds to the shape of the preform that is to be made, draping which consists in superposing layers or plies of two-dimensional fiber fabric on a former matching the shape of the preform to

be made, the superposed plies optionally being bonded together by needling or by stitching, or indeed by three-dimensional weaving or knitting.

The preform can be densified in well-known manner using a liquid process or a gas process. Liquid process densification consists in impregnating the preform - or in pre-impregnating the yarns or plies making it up - with a matrix precursor, e.g. a carbon or ceramic precursor resin, and in transforming the precursor by heat treatment. Gas densification, known as chemical vapor infiltration, consists in placing the preform in an enclosure and in admitting a matrix-precursor gas into the enclosure. Conditions, in particular temperature and pressure conditions, are adjusted so as to enable the gas to diffuse into the core of the pores of the preform, so that on coming into contact with the fibers it forms a deposit of matrix-constituting material thereon by one of the components of the gas decomposing or by a reaction taking place between a plurality of components of the gas.

For pieces that are of relatively complex shape, for example bowl shaped, a particular difficulty lies in making a fiber preform having the right shape.

Another difficulty lies in obtaining densification in a manner that is reasonably simple and fast, in particular for bowls of large dimensions. Unfortunately, in the semiconductor industry, there exists a need for silicon ingots of ever greater diameter, thus requiring crucibles and support bowls to be provided that are of corresponding dimensions.

Object and summary of the invention

An object of the invention is to propose a method of manufacturing a bowl of thermostructural composite material that makes it possible to overcome the above difficulties, while remaining simple and low in cost.

According to the invention, the method comprises the steps which consist in:

· making a bowl preform by winding a yarn, the preform having an axial passage through its bottom;

· densifying the bowl preform by chemical vapor infiltration; and

· closing the passage by means of a plug.

Making a bowl preform with an axial passage presents two advantages. Firstly, the preform can be made by winding yarn without special difficulty. This would not be the case if a complete bowl preform had to be obtained by winding the yarn. In addition, while the preform is being densified by chemical vapor infiltration, the presence of an axial hole enhances flow of the gas and thus enhances densification.

A stiffened or consolidated bowl preform is preferably obtained prior to performing densification by chemical vapor infiltration. In conventional manner, a consolidated bowl preform is made by partial densification of a fiber structure having the desired shape, with the partial densification being at least sufficient to enable the preform to be handled. Partial densification can be performed by a gas process, or it can be performed by a liquid process, using impregnation by means of a precursor of the material that constitutes the matrix of the composite material, and transforming the precursor by heat treatment.

The perform can be consolidated by impregnation with a carbon precursor, e.g. selected from phenolic, furan, epoxy, and polyimide resins, and then transforming the precursor.

A consolidated preform is advantageously made by winding a yarn impregnated with said precursor.

Two consolidated preforms can be made simultaneously on a mandrel of a shape that corresponds to that of two facing bowl portions, with the yarn being wound over the

mandrel and with the resulting winding being cut in its middle portion.

Densifying the preform by chemical vapor infiltration makes it possible to obtain a carbon matrix having the continuity necessary to ensure that the installation for producing a silicon single crystal is not polluted with particles that come from the fibers or from resin coke formed on the fibers in order to consolidate the preform. A carbon matrix obtained by chemical vapor infiltration also presents better ability to withstand corrosion on coming into contact with a quartz crucible at high temperature.

Advantageously, the consolidated bowl preform is made from yarn that has no surface treatment, e.g. oxidation under controlled conditions using electrochemical or other means. In particular, the yarn can be a carbon yarn. The absence of the surface treatment which is usually provided on commercially-available yarns for providing surface functions that encourage bonding with organic matrices contributes to obtaining better dimensional stability by avoiding the appearance of internal stresses while making the composite material.

In another feature of the method, the method includes a step which consists in performing a final chemical vapor infiltration step after the passage has been closed by the plug, with the plug itself preferably being made of thermostructural composite material. The final infiltration step can include forming a matrix of a kind that is different from that formed previously during the steps of consolidating the bowl preform and the subsequent densification thereof. Thus, with a carbon densified preform, the final infiltration step can consist in depositing a ceramic matrix, e.g. of silicon carbide. Such an outer matrix material provides the composite material with protection against oxidation.

Advantageously, the bowl is subjected to high temperature purification and stabilization treatment, preferably at a temperature greater than 2200°C. Purification can be performed under an atmosphere of chlorine, as is well known for graphite. It makes it possible to remove impurities that might pollute the silicon when using the bowl as a support for crucibles containing silicon for manufacturing single crystal silicon ingots.

Such purification treatment can be performed on the consolidated bowl preform. The heat treatment then also contributes to avoiding dimensional variations during the subsequent manufacturing processes. Providing the plug closing the bottom of the bowl has also been subjected to purification treatment, performing purification after chemical vapor infiltration need not be necessary.

A protective coating can be formed at least on the inside of the bowl. Such a coating can be of pyrolytic carbon or "pyrocarbon", obtained by chemical vapor deposition, or it can be of ceramic, e.g. silicon carbide (SiC) likewise obtained by chemical vapor infiltration. In a variant, the inside face of the bowl can be provided with a protective layer, e.g. made of C/C composite material.

Brief description of the drawings

The invention will be better understood from the following detailed description given with reference to the accompanying drawings, in which:

· Figure 1 is a highly diagrammatic half-section view showing a bowl of composite material used as a crucible support in an installation for producing silicon ingots;

· Figure 2 is a flow chart showing the successive steps in a first implementation of a method in accordance with the invention; and

· Figures 3A to 3D are half-section views showing successive steps in making a bowl of composite material using the method of Figure 2.

Detailed description of implementations

As already mentioned, the field to which the invention applies is more particularly that of making bowls of thermostructural composite material for supporting crucibles in installations that produce single crystal silicon ingots.

Highly diagrammatic Figure 1 shows such a bowl of composite material, e.g. C/C composite material supporting a crucible 5 which is usually made of quartz. The bowl 1 stands on an annular support formed with a ring 2 mounted at the end of a shaft 3 having a setback 4 therein. The bowl has a bottom portion 1a and a surround portion 1b, part of which is substantially cylindrical and is connected to the bottom portion via a region of rounded profile. The bottom portion of the bowl 1 is machined so as to form a centering bearing surface corresponding to the setback 4 and a support surface on the ring 2.

After the crucible has been filled with silicon, the assembly is placed in a furnace and the temperature in the furnace is raised to a value which is high enough to cause the silicon to liquefy. At this temperature, the crucible softens and it matches the shape of the bowl. A germ having a desired crystal arrangement is then brought into contact with the bath of silicon and is extracted slowly therefrom, thereby forming a column between the germ and the bath. An ingot is thus drawn at very low speed, and its length can lie in the range 1 meter (m) to 2 m.

That method of manufacturing silicon ingots is well known and does not form part of the invention, such that a more detailed description is not required.

Because thermostructural composite materials have the ability to conserve good mechanical properties and good dimensional stability at high temperatures, they are particularly suitable for making bowls for use in the above application.

The description below relates more particularly to making bowls out of C/C composite materials with carbon fiber reinforcement and a carbon matrix, or at least a matrix that is essentially made of carbon. The invention also covers making bowls out of CMC type composite materials, i.e. having ceramic fiber reinforcement (e.g. made of SiC fibers) and a matrix that is also ceramic (e.g. likewise of SiC), where technologies for making CMCs are well known.

The fiber reinforcement is made from yarns of the kind commercially available but free from any of the surface treatment normally provided to provide surface functions that encourage bonding with an organic matrix when such yarns are used to form fiber/resin type composite materials that are not intended for high temperature applications. The absence of surface functions makes it possible to avoid internal stresses during the process of manufacturing the composite material using the method of the invention.

A first implementation of a method of manufacturing a bowl of composite material is described below with reference to Figures 2 and 3A to 3D.

A first step 10 of the method (Figure 2) consists in providing a mandrel 12 (Figure 3A). The shape of the mandrel corresponds to the shape of the two parts of the outlines of the bowls that are to be made placed rim-to-rim. At its axial ends, the mandrel is associated with rings 14 which leave an annular gap 16 formed in the outside surfaces thereof at the periphery.

By way of example, the mandrel 12 and the rings 14 can be made of metal. The assembly is mounted and prevented from moving axially on a shaft 18 which passes

through central passages of the rings 14 and is connected to a rotary drive motor (not shown).

A second step 20 in the method consists in winding a yarn onto the mandrel 12.

The winding 22 is made using a yarn that is pre-impregnated with a liquid precursor of carbon, e.g. a phenolic resin. At the axial ends of the mandrel, the winding extends far enough to be wound in part around the rings 14 in the vicinity of the recesses 16. Winding is continued so as to build up the thickness desired for the preforms that correspond to the bowl outline portions that are situated rim-to-rim (Figure 3B). The rings 14 make it easier to stop winding yarn at the axial ends of the winding. The rings 14 can be formed integrally with the mandrel 12. In order to avoid having excessive winding thickness in the vicinity of the end zones of the mandrel where diameter drops off quite quickly, winding can include a plurality of steps 24', 24", ..., at different diameters.

After winding, the blank 26 formed by the winding 22 and supported by the mandrel 12 is placed in an oven to polymerize the phenolic resin impregnating the yarn of the winding (step 30 of the method).

At the following step 40, the blank 26 is cut in half radially so as to obtain two half-shells 28 which are withdrawn from the mandrel 12 (Figure 3C), each half-shell having an axial passage 30.

Each half-shell 28 is then subjected to heat treatment (step 50) so as to carbonize the phenolic resin and obtain a consolidated bowl preform having an axial passage 30 through its bottom. The yarn winding is consolidated by being densified with a carbon matrix derived from transforming the phenolic resin. This provides a preform that is densified in part, i.e. that still presents accessible residual porosity, while nevertheless having sufficient strength to be handled.

Thereafter, the purified bowl preform is placed in an enclosure to be subjected to a step of densification by chemical vapor infiltration (step 60 of the method). Densification is performed to fill in, at least in part, the residual porosity in the consolidated preform with pyrolytic carbon. This is achieved in a manner that is well known in itself using a gas containing a hydrocarbon, such as methane or natural gas, constituting a precursor for the carbon.

A plurality of bowl preforms can be densified simultaneously within the same enclosure. To this end, the preforms are placed one above another, in axial alignment with gaps being left between them to allow the gas to flow. A method of chemical vapor infiltration with directed gas flow as described in US patent No. 5 904 957 can be used.

The step 60 of chemical vapor infiltration contributes not only to finishing off preform densification, but also to forming a continuous matrix of controlled microstructure that is capable of holding within the material any carbon particles from the fibers or grains of coke from the consolidating resin, such that there is no danger of these particles or grains giving rise to pollution when the bowl is in use. Compared with a carbon matrix as obtained using a liquid process, the carbon matrix obtained by chemical vapor infiltration also provides better resistance to corrosion on contact with a quartz crucible at high temperature.

The following step 70 of the method consists in machining the bottom portion of the bowl so as to fix a plug 34 that closes the passage 30 (Figure 3D). In the example shown, the plug 34 is made of two pieces 35 and 37, e.g. of C/C composite material (step 80) that have been subjected if necessary to a step of purifying the carbon. The piece 35 is saucer-shaped and its periphery forms a lip 35a that bears against the rim of the passage 30, on the inside of the bowl, while the piece 37 which

is also saucer-shaped has a rim 37a which bears against the rim of the passage 30 on the outside. The pieces 35 and 36 can be bonded together by screw fastening, with the piece 35 presenting a projecting central portion which is screwed into a housing in the piece 37. The pieces 35 and 37 clamp the rim 30a of the opening 30. The pieces 35 and 37 constituting the C/C composite material plug 34 can be made by any known method. For example, preforms can be made by superposing two-dimensional plies in the form of carbon fiber disks. The plies which can be woven cloth, for example, are bonded together by needling or by stitching. Thereafter they can be densified by means of a carbon matrix using a liquid process or by chemical vapor infiltration.

After the plug 34 has been installed (step 90) a new and final densification step 100 is performed using chemical vapor infiltration to provide final carbon matrix so as to ensure that the plug 34 is securely assembled to the bottom proton of the preform 28 and so as to finish off densification thereof. A C/C composite material bowl 36 is thus obtained ready for use, possibly after a final stage of machining to finish the bottom and plug portion 34.

The following step 110 of the method consists in purifying the carbon of the resulting bowl when the intended application requires the bowl to be free from impurities. This applies to installations for drawing a silicon single crystal for use in manufacturing semiconductor products, in which the silicon must initially be uncontaminated by any impurities. The carbon can be purified by heat treatment at a temperature that preferably lies in the range 2200°C to 3000°C, e.g. a temperature equal to about 2400°C, under a non-oxidizing atmosphere, e.g. under an atmosphere of chlorine, and at a pressure that is preferably less than 100 kiloPascals (kPa) for example is equal to about 10 kPa. Such heat treatment under chlorine is well known

in itself for purifying graphite. The heat treatment also serves to stabilize the dimensions of the consolidated bowl preform. In a variant, purification could be performed once the bowl preform has been consolidated, after step 50. Insofar as the plug 34 has also been subjected to purification, the final purification step after chemical vapor infiltration could then be omitted.

When the bowl is for receiving a quartz crucible, it can be desirable to protect the bowl from erosion caused by a chemical reaction between quartz (SiO_2) and the carbon of the bowl at the temperature at which the crucible is used. When drawing a single crystal of silicon, the crucible is raised to a temperature of about 1600°C at which quartz becomes soft, is subject to creep, and fits closely to the shape of the supporting bowl, while also tending to become reactive.

Protection can be obtained by forming a protective coating (step 120) at least on the inside of the bowl. The protective coating can be of pyrolytic carbon or "pyrocarbon" obtained by chemical vapor deposition, or it can be made of ceramic, e.g. silicon carbide (SiC) likewise obtained by chemical vapor infiltration. In a manner that is well known per se, an SiC deposit can be obtained by chemical vapor deposition using a gas that contains a precursor of SiC, such as methyltrichlorosilane (MTS).

The protective coating can be formed continuously running on from the final densification step 100, prior to any final heat treatment step for purification.

In a variant, the bowl can be protected by interposing an intermediate layer between the bowl and the crucible, said layer matching the shape of the bowl, e.g. being a protective layer of a thermostructural composite such as a C/C composite obtained by densifying a fiber preform constituted by a carbon felt or by two-dimensional plies of carbon fibers.

Figure 1 shows such a protective layer 6 lining the inside face of the bowl 1. This protective layer is consumable, and the bowl is re-lined periodically.

Although a description above relates to winding a blank suitable for making two bowl blanks simultaneously, the bowl blanks could naturally be made individually.

CLAIMS

1/ A method of manufacturing a bowl of thermostructural composite material formed by fiber reinforcement densified by a matrix, the method being characterized in that comprises the steps consisting in:

· making a bowl preform (28) by winding a yarn, the preform having an axial passage (30) through its bottom;

· densifying the bowl preform by chemical vapor infiltration; and

· closing the passage by means of a plug (34).

2/ A method according to claim 1, characterized in that a consolidated bowl preform is made prior to chemical vapor infiltration.

3/ A method according to claim 1 or claim 2, characterized in that the consolidated bowl preform (28) is made by winding a yarn impregnated by a precursor for said material constituting the matrix, and by transforming the precursor by heat treatment.

4/ A method according to claim 3, characterized in that the consolidated bowl preform (28) is made by winding a yarn impregnated by a carbon precursor and by transforming the precursor.

5/ A method according to claim 4, characterized in that the carbon precursor is selected from phenolic, furan, epoxy, and polyimide resins.

6/ A method according to any one of claims 3, 4, and 5, characterized in that two consolidated preforms are made simultaneously by winding a shape on a mandrel (12) where the shape corresponds to that of two bowl outline portions joined rim-to-rim, and by cutting the resulting winding (22) in its middle portion.

7/ A method according to any one of claims 1 to 6, characterized in that the bowl preform is made from yarn that has no surface treatment to provide surface functions.

8/ A method according to any one of claims 1 to 7, characterized in that the bowl preform is made from a carbon yarn.

9/ A method according to any one of claims 1 to 8, characterized in that the bowl is subjected to high temperature purification and stabilization treatment.

10/ A method according to any one of claims 1 to 8, characterized in that the high temperature purification and stabilization treatment is performed on the consolidated bowl preform.

11/ A method according to claim 9 or claim 10, characterized in that the purification and stabilization treatment is performed at a temperature greater than 2200°C.

12/ A method according to any one of claims 1 to 11, characterized in that bowl preform densification is performed by forming a carbon matrix.

13/ A method according to any one of claims 1 to 12, characterized in that the plug (34) is made in two pieces (35, 37) that are assembled together so as to clamp onto the rim of the axial passage in the preform.

14/ A method according to any one of claims 1 to 13, characterized in that the passage (30) is closed by a plug (34) made of thermostructural composite material.

15/ A method according to any one of claims 1 to 14, characterized in that it includes a step consisting in performing a final chemical vapor infiltration step after the passage (30) has been closed by the plug (34).

16/ A method according to claim 15, characterized in that the final chemical vapor infiltration step comprises forming a ceramic matrix phase.

17/ A method according to claim 16, characterized in that the ceramic matrix phaseis made of silicon carbide.

18/ A method according to any one of claims 1 to 17, characterized in that a protective coating is formed at least on the inside face of the bowl.

19/ A method according to claim 18, characterized in that a protective coating is made out of pyrolytic carbon.

20/ A method according to claim 18, characterized in that a protective coating is made out of silicon carbide.

21/ A method according to any one of claims 1 to 20, characterized in that the inside face of the bowl is provided with a protective layer.

22/ A method according to claim 21, characterized in that the protective layer is made of a thermostructural composite material.

23/ A method according to claim 22, characterized in that a plurality of consolidated bowl preforms are densified simultaneously by chemical vapor infiltration.

A B S T R A C T

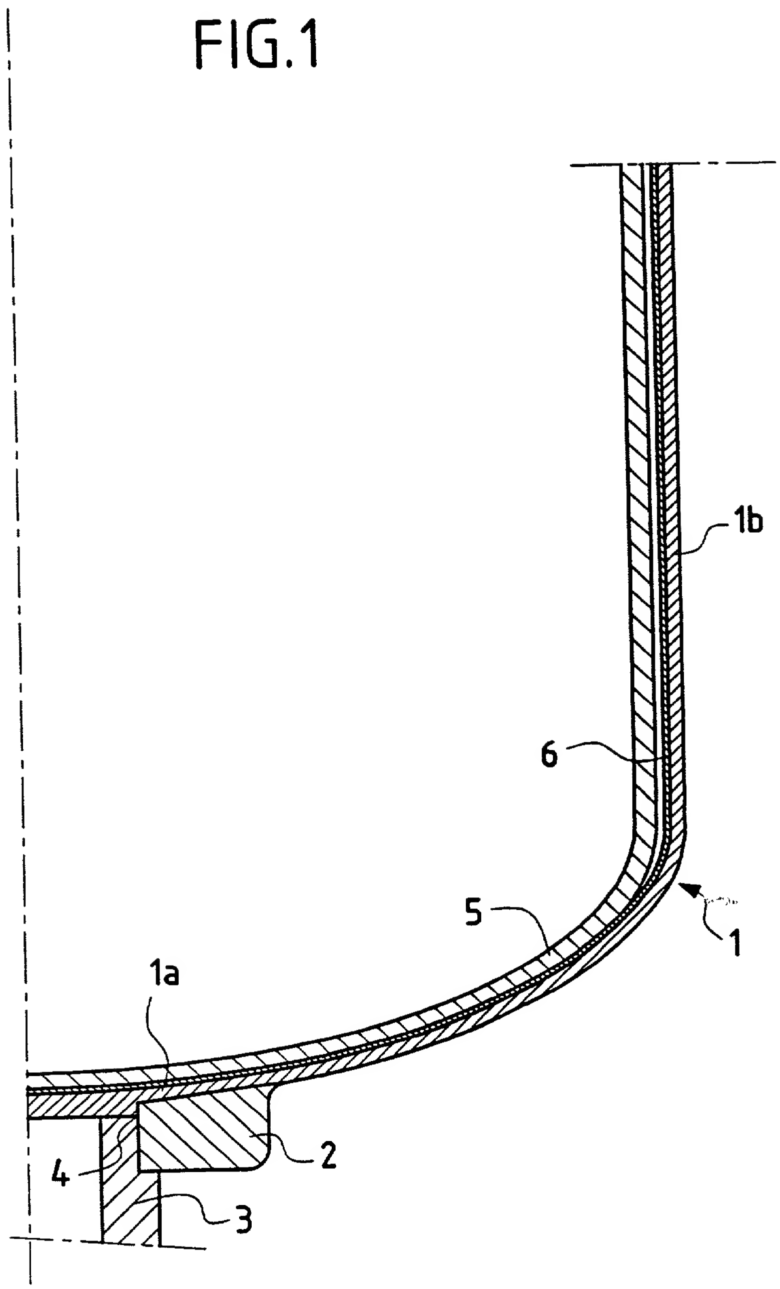
A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, IN PARTICULAR FOR AN INSTALLATION THAT PRODUCES SILICON SINGLE CRYSTALS.

A composite material bowl 36 comprising fiber reinforcement densified by a matrix is made by winding a yarn on a preform 28 having an axial passage 30 through its bottom, densifying the preform by chemical vapor infiltration, and closing the passage by a plug 34. Prior to densification, the preform can be consolidated. A final chemical vapor infiltration step can be performed after the plug has been put into place.

Translation of the title and the abstract as they were when originally filed by the Applicant. No account has been taken of any changes that may have been made subsequently by the PCT Authorities acting ex officio, e.g. under PCT Rules 37.2, 38.2, and/or 48.3.

09/889860

FIG.1



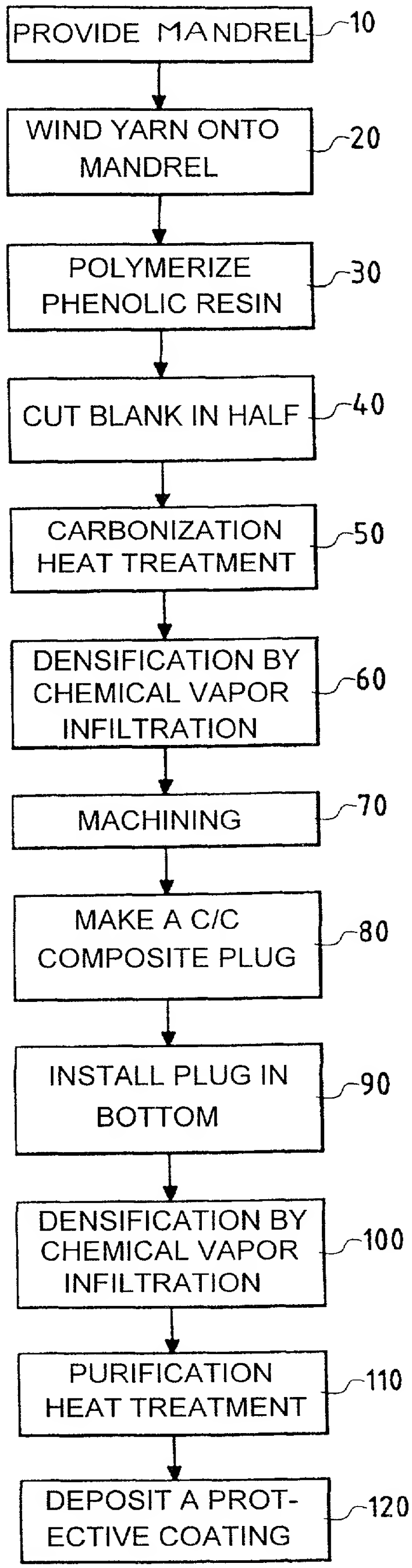

PROVIDE MANDREL
10
WIND YARN ONTO MANDREL
20
POLYMERIZE PHENOLIC RESIN
30
CUT BLANK IN HALF
40
CARBONIZATION HEAT TREATMENT
50
DENSIFICATION BY CHEMICAL VAPOR INFILTRATION
60
MACHINING
70
MAKE A C/C COMPOSITE PLUG
80
INSTALL PLUG IN BOTTOM
90
DENSIFICATION BY CHEMICAL VAPOR INFILTRATION
100
PURIFICATION HEAT TREATMENT
110
DEPOSIT A PROT-ECTIVE COATING
120

FIG.2

FIG.3A

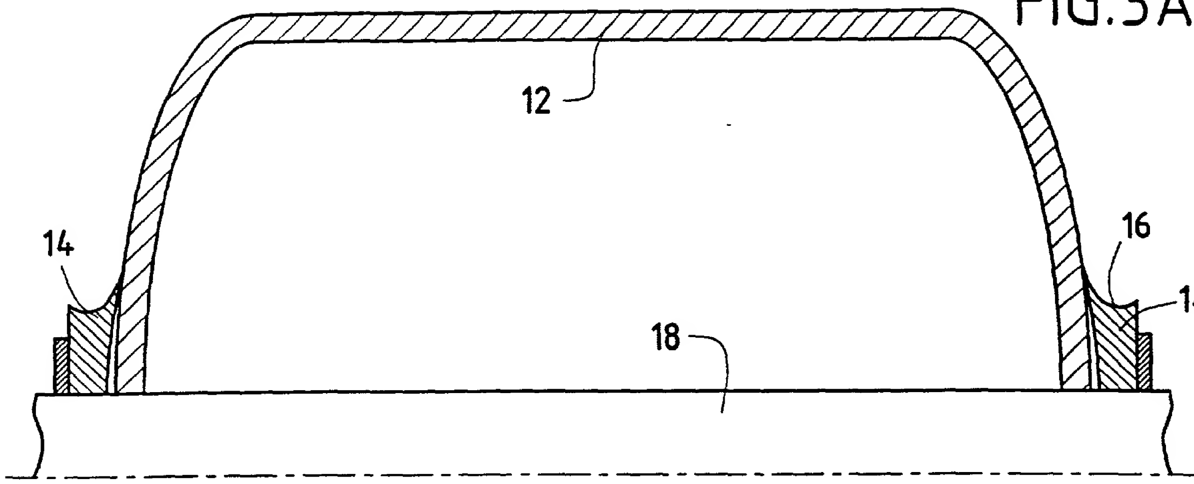
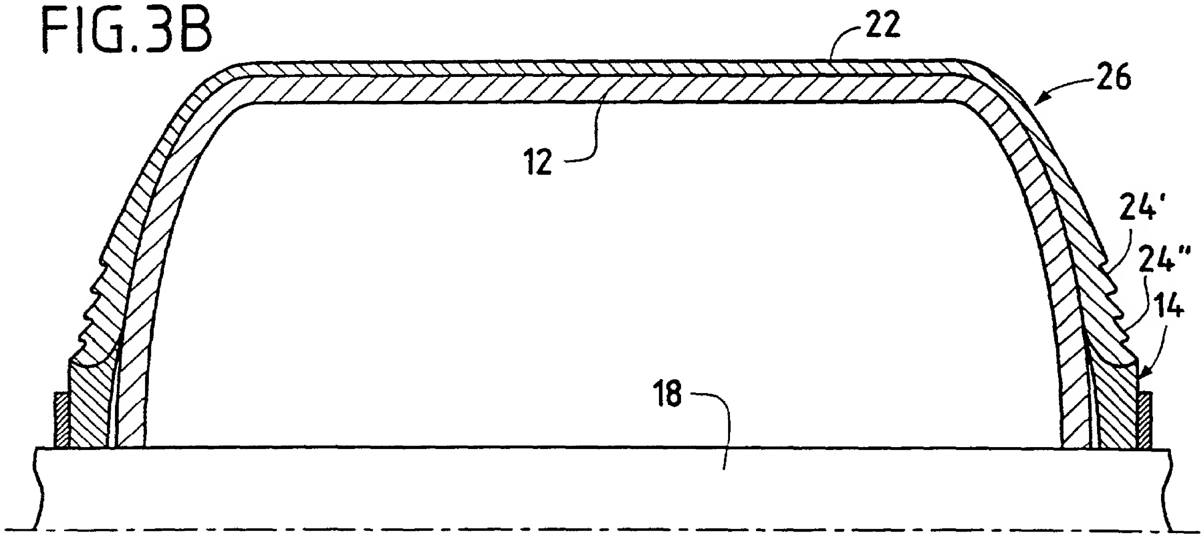


FIG.3B



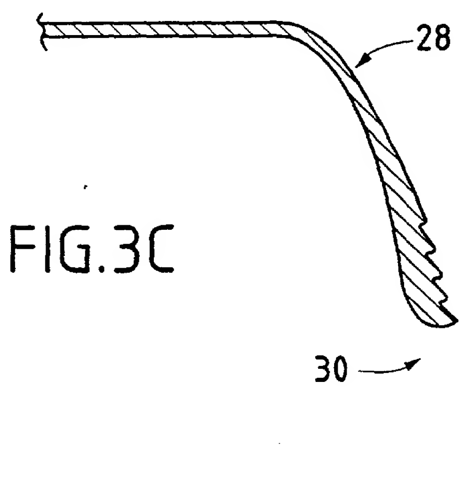


FIG.3C

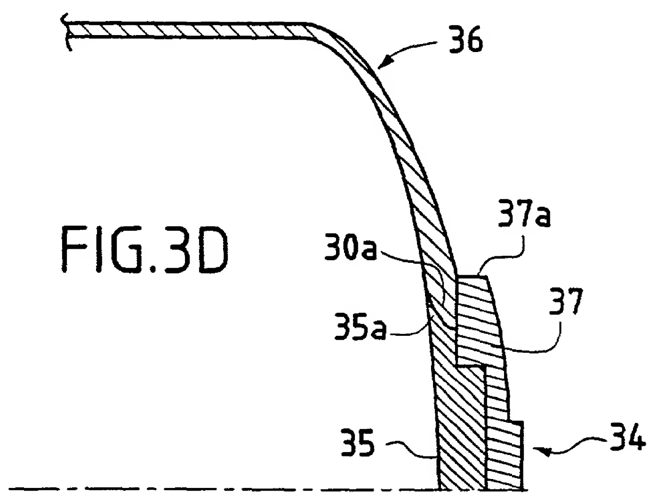


FIG.3D

Attorney
Docket No.: BDL-341XX

DECLARATION AND POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: A method of manufacturing a thermostructural composite material bowl, in particular for an installation that produces silicon single crystals.

the specification of which (check one):

[x] is attached hereto. [ ] was filed ________ as Application No.____________ amended on ______________(if applicable).

[ ] was filed as PCT International Application No. PCT/FR00/03275 on November 24, 2000 and was amended under PCT Article 19 on ______________ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, USC §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)		Date Filed	Priority Claimed	
99 14766	FRANCE	24 November 1999	[x]	[ ]
(Number)	(Country)	(Day/Month/Year)	Yes	No
			[ ]	[ ]
(Number)	(Country)	(Day/Month/Year)	Yes	No

I hereby claim the benefit under Title 35, USC §119(e) of any United States provisional application(s) listed below:

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

Express Mail Number

EL 751779448 US

Attorney
Docket No.: BDL-341XX

I hereby claim the benefit under Title 35 USC §120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 USC §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business connected therewith in the Patent and Trademark Office, and to file with the USRO any International Application based thereon.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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CLG:mes/221588